Nanoscale Analysis of Impurity Distribution in Silicon Devices by Atom Probe Tomography

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論 文 内 容 要 旨

Over the past decades, the scale of the silicon (Si)-based Metal-Oxide-Semiconductor Field-Effect Transistors (MOSFETs) is continually shrinking to about 10 nm regime. The function of the MOSFET devices is determined by the cooperated impurities, including dopants (boron, phosphorus, etc.) and other impurities (hydrogen, oxygen, carbon, etc.), continuous shrinking of device scale requires a better control of the impurity distribution, i.e. the nanoscale confinement of the impurities.

There are several methods to confine the impurity distribution, such as (1) Co-doping: adding a supplementary element can be used to control the principle dopant element. This method is usually used for controlling the in-depth diffusion of the principle dopant. For example, C co-implantation can be used to suppress P and B diffusion in crystalline Si. B co-doping is able to suppressed the As diffusion along the grain boundaries of polycrystalline Si. (2) Blocking layer: using a special layer to prevent the penetration of unwanted impurities into the protected region. For example, using a tungsten mixed cobalt layer could be used to prevent copper diffusing from the Cu-interconnect. (3) Lithography mask: lithography is a typical method to control the lateral range of the dopants and the resolution of lithography relies on the wavelength of incident beam. The resolution of lithography relies on the wavelength of incident beam. The light source for photolithography used to be visible light, ultraviolet (UV) light, extreme UV light. Electron beam could be accelerated to decrease its wavelength to less than 1 nm.

For realizing the confinement of impurities, we need to clarify their behaviors and the mechanisms responsible for the behaviors. In order to understand the mechanisms, the visualization of the elemental distribution in nanoscale region with atomic resolution is the precondition. Therefore, the research purpose of current work is：(1) visualization of the impurity distribution in the nanoscale region, and (2) understanding of the mechanisms of impurities behavior.

Recently, atom probe tomography (APT) has emerged as a powerful technique for its capability of obtaining 3D elemental

distribution maps with nearly atomic scale resolution. In preparation for APT measurements, samples are fabricated into a needle shape, and the application of a focused ion beam (FIB) enables the site-specific extraction of the region of interest during the needle fabrication process. The implementation of pulsed lasers has enabled its application to semiconductor materials.

In current thesis, APT will be mainly used to study several topics to achieve a better understanding on the impurities behavior and the mechanisms. Such a study will provide very important information for the further confinement of impurities and finally enhance the performance and reliability of future nano-electronic devices.

Corresponding to the three typical methods on impurities confinement, three interesting topics are investigated in current thesis:

1. Effect of coimplanted carbon (C) on boron (B) behaviors. B is the principle *p*-type doping elements in silicon (Si), and its behavior is vital to the performance of the semiconductor devices. On one hand, transient enhanced diffusion (TED) of B during the post-implantation annealing is an obstacle to restrict the junction depth. On the other hand, it is believed that B and *I* form clusters in the high concentration region of the implanted profile, which is responsible for the low electrical activation rate. C coimplantation is proposed as an effective method to suppress B diffusion but the mechanism is still unclear.

APT is promising to demonstrate behavior of B and B-C interaction. However, the APT analysis on B distribution may be biased due to the laser irradiation during the measurement. Before our experiment on investigating the B behavior and B-C interaction, we studied the possible artifacts induced by high power laser and optimized the laser condition. The measured distributions are almost uniform and homogeneous when using low laser power, while clear B accumulation at the low-index pole of single-crystalline Si and segregation along the grain boundaries in polycrystalline Si are observed when using high laser power (100 pJ). These effects are thought to be caused by the surface migration of atoms, which is promoted by high laser power. In the following experiments, we selected 30 pJ so as to avoid introducing artifacts as well as achieve high success rate of the measurements.

Consequently, we use secondary ion mass spectrometry (SIMS) and APT to to investigate the effects of carbon (C) co-implantation and subsequent annealing at 600 to 1200 °C on the behavior of implanted boron (B) atoms in silicon. When B alone was implanted, annealing at 600 to 800 °C caused it to form clusters in the peak region (10^{20} cm^{-3}) of the concentration profile, and diffusion only occurred in the low-concentration tail region (< 10^{18} cm^{-3}), which is thought to be the well-known transient enhanced diffusion. However, when co-implantation with C was performed, this diffusion was almost completely suppressed in the same annealing temperature range. In the absence of C implantation, annealing at 1000 °C caused B clusters to begin to dissolve and B to diffuse out of the peak concentration region. However, this diffusion was also suppressed by C implantation because C atoms trapped B atoms in the kink region. At 1200 °C, B clusters were totally dissolved and strong B diffusion occurred. In contrast to lower annealing temperatures, this diffusion was actually enhanced by C implantation. It is believed that Si interstitials play an important role in the interaction between B and C. This kind of comprehensive investigation yields important information for optimizing ion implantation and annealing processes.

2. Blocking of H penetration in Al_2O_3/HfO_2 high-*k* stacks. High-permittivity (high-*k*) materials based on hafnium dioxide (HfO_2) have been widely used as gate dielectrics in logic devices. Hydrogen (H) plays an important role in determining the reliability and performance of HfO_2- and Al_2O_3-based high-*k* dielectric electronic devices. Alumina (Al_2O_3) has been reported as a potential H_2 diffusion barrier for preventing H attack but this has not been directly demonstrated.

APT is a useful method to study the distribution of ion in nanoscale region, thus it is widely used to study the trapping or blocking effect. However, H detection is a problem in APT due to the residual gas in the analysis chamber. In order to avoid the interference from residual gas, deuterium (D), an isotope of H, was introduced into the poly-Si cap of $Al_2O_3/Hf_xSi_{1-x}O_2/SiO_2$ high-*k* stacks by ion implantation. APT was then used to image the D distribution in samples annealed under different conditions. The results clearly demonstrated that the D atoms were trapped at the interface of poly-Si and Al_2O_3 after annealing at 900 K for 10 min. Thus, it is possible that Al_2O_3 blocks the H atoms at the surface, preventing them from diffusing into the high-*k* dielectrics during the H_2 annealing process in current fabrication technology. The current work also exhibits an example of investigating H behavior in semiconductors by APT.

3. Distribution of ions implanted through nanoapertures. Implantation of dopant ions through a resist mask with nano-apertures is a method to realize a deterministic uniform dopant distribution. Electron beam lithography (EBL) is a potential technique for sub-10 nm device fabrication. The distribution of ions near a mask edge is critical for device performance, but measuring the doping profiles in such a small region is very difficult.

APT is first-ever used to investigate the 3D distribution of germanium atoms in Si after implantation through nano-aperture of 10 nm in diameter, for evaluation of the amount and spatial distribution of implanted dopants. Since it is difficult to maintain an intact distribution spot in the needle specimen due to the limited precision of the FIB technique. Therefore, the best results were selected from dozens of replicate trials. Meanwhile, we performed a simulation to show the expected dopant distribution. The experimental results obtained by APT are generally consistent with a simple simulation with consideration of several effects during lithography and ion implantation, such as channeling and resist flow.

Fabrication of nanoscale semiconductor devices is based on the precise placement of dopant atoms into the crystal lattice of semiconductors. Throughout the fabrication processes like lithography, ion implantation, and thermal annealing, fundamental phenomena like dopant diffusion, trapping, and clustering occur simultaneously. These processes are described by atomic scale mechanisms of impurity-defect-host interaction and have an immense impact on the electrical performance of the devices.

In this work, we demonstrated the application of APT on investigating the nanoscale distribution and behavior of impurities in Si devices under different conditions, and speculated the mechanisms responsible for such behaviors. The results in current study, which are hard to obtain by other techniques, provide important information for optimizing the manufacturing process in the semiconductor industry. Except for its application, we also studied on the APT technique itself. We studied the possible artifacts induced by high power laser, and we try to introduce D into the samples for avoid the residual gas problem. Such kind of studies are very helpful for improving this technique for future application on semiconductor industry.

Monitoring and controlling the atomic scale impurity-defect-host interaction is required for the confinement of impurities in nanoscale region, which is necessary for proceeding the development of IC technology. From this perspective, APT, combined with other characteristic techniques, will play an increasingly important role on contributing to semiconductor industry.

論文審査結果の要旨

シリコンデバイスは、長年、微細化の壁が訪れるといわれて久しいが、現在でもさらなる微細化が進んでいる。しかしながら、そのために解決すべき問題は年々困難になり、今、最も必要とされていることの一つは、不純物や添加元素をナノスケールの精度でコントロールする技術とそのための不純物や添加元素の振る舞いを理解することである。Tu Yuan 君は、最近開発されたレーザー補助３次元アトムプローブと呼ばれる最新の分析手法を駆使して、これに関連する以下に述べる研究成果をあげた。

３次元アトムプローブ法とは、針状の試料に高電圧を印加することによって原子をイオン化して１個１個剥ぎ取り、それを位置敏感検出器で検出することによって、原子スケールの分解能で元素分布を３次元的に分析できる手法である。最近、パルスレーザーを照射することにより半導体や絶縁性材料にも幅広く応用できることがわかり、非常に注目されている。しかしながら、3 次元アトムプローブ法では、シリコン中では、ホウ素の検出において測定法特有の問題があることがわかってきた。Tu 君は、このような問題を回避するための測定条件を見いだし、ホウ素の拡散挙動、特に、炭素と共注入した場合のホウ素単独注入との違い、ホウ素のクラスタリングの形成・解離過程・安定性を初めて明らかにした。また、シリコンデバイス中で様々な問題を引き起こす水素が、シリコン／アルミナ薄膜層界面に捕獲され、内部に拡散することを抑制することを明らかにした。さらに、均一な不純物注入で最近注目されている、ナノホールを通して注入されたイオンがシリコン中でどのような分布をするのか、実験的に初めて測定に成功した。これらの知見は、将来のデバイス開発にとっての重要な基礎的知見であるとともに、3 次元アトムプローブ法の応用範囲を様々な新規デバイスに広げたという意味に置いても重要な進歩である。

本論文成果の発表は、学術専門誌掲載論文６編（内第一著者３編）、国内学会発表３回（応用物理学会ポスター賞１回）、国際会議発表３回を数えており、彼の研究は国内外で高く評価されている。

本論文は、直接的には半導体デバイス分野への大きな貢献を果たしているが、用いた手法は量子ビームを利用した高度な分析であること、また、イオン注入等によって形成される照射欠陥の役割や、それに付随する微量不純物の振る舞いなど、原子力材料を含んだ様々な材料にも共通の重要な学理を数多く含み、量子エネルギー工学にとっても大きな業績といえる。

よって、本論文は博士(工学)の学位論文として合格と認める。